



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 253 539
A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 87305828.3

(51) Int. Cl.4: **B05B 5/08**

(22) Date of filing: **01.07.87**

(33) Priority: **17.07.86 GB 8617527**

(43) Date of publication of application:
20.01.88 Bulletin 88/03

(54) Designated Contracting States:
AT BE CH DE ES FR GB IT LI NL SE

(71) Applicant: **IMPERIAL CHEMICAL INDUSTRIES PLC**
Imperial Chemical House Millbank
London SW1P 3JF(GB)

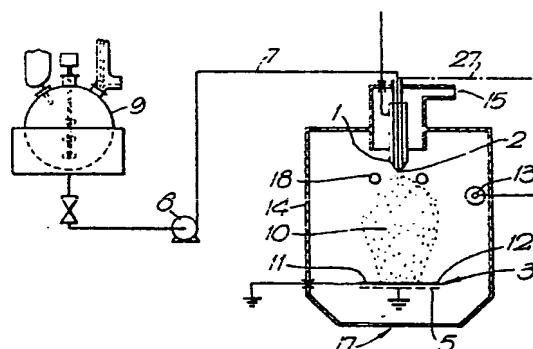
(72) Inventor: **Head, Robert Arthur**
48 Appleton Road
Upton Near Chester(GB)
Inventor: Orton, Michael Leslie
24 School Lane
Hartford Northwich(GB)
Inventor: Robinson, Christopher Lawton
5 Ambleside Close Beechwood West
Runcorn Cheshire(GB)

(73) Representative: **Draggett, Peter Thornton et al**
Imperial Chemical Industries PLC P.O. Box 6
Bessemer Road
Welwyn Garden City Herts AL7 LHD(GB)

(54) Spraying process.

(57) A process for the spray application of a fluid which is an adhesive or surface coating or a precursor thereof, characterised by supplying such a fluid to a sprayhead and applying an intense electrical field to the fluid such that the fluid moves from the sprayhead under the influence of the field to form a spray, the field being intensified by means of a charged electrode adjacent to the sprayhead.

Fig. 1.



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SPRAYING PROCESS

This invention relates to the application of adhesives and surface coatings, in particular reactive adhesives and coatings by electrostatic spraying, and to production lines utilising such application methods.

In known electrostatic spraying of non-reactive materials liquid introduced via a charged spray nozzle into a relatively intense electric field produces charged fibres or droplets which tend to move towards earth and these may be collected on a suitable substrate which may be a field electrode or other than the field electrode.

From UK 1,569,707 it is known to place an earthed 'field intensifying electrode' adjacent to the sprayhead, which may advantageously reduce the necessary operating potential and thus reduce current loss through corona discharge from the sprayhead. Spraying using apparatus of this type is referred to hereinafter as 'electrodynamic spraying'.

As is disclosed in UK 1,569,707 a typical 'adjacent' electrode with a typical sprayhead working potential of 20 KV is mounted at about 20 mm from the sprayhead and is thus very different from conventional auxiliary electrodes used in electrostatic spraying.

The industrial application of adhesives and surface coatings, for example in production lines for packaging, parts assembly (such as shoes and aero and boat frames) or surgical dressings and drapes, generally requires accuracy and economy of application, which necessitates contact application methods.

Additionally, known production lines need relatively high throughput rates for economic operation, requiring fast-set/-cure adhesives or coatings. Contact application does not generally help desirable speeds to be achieved.

Reactive adhesives or coatings are often multicomponent, so that they are not conveniently mixed in contact application, or require special and costly curing procedures. Rapidly reacting room temperature multicomponent systems react too rapidly to be contact applied. As a solution to this problem for packaging adhesives, hot melt (rapid set) adhesives are used, but these require wasteful heating processes.

Surprisingly, we have now found a method of spray application of adhesives and surface coatings which combines the accuracy of contact application with the speed of spray application. This method is especially useful for rapidly reacting room temperature multicomponent systems in achieving adequate component mixing and convenient application.

Thus the present invention provides a process for the spray application of a fluid which is an adhesive or a surface coating or a precursor thereof characterised by the electrodynamic spraying of the fluid, preferably a reactive fluid. That is, characterised by supplying such a fluid to a sprayhead and applying an intense electrical field to the fluid such that the fluid moves from the sprayhead under the influence of the field to form a spray, the field being intensified by means of a charged electrode mounted adjacent to the sprayhead.

The fluid may be the adhesive or surface coating or a precursor thereof or a solution, dispersion or suspension thereof or, less favourably, a melt. It may be a single fluid or a reactive precursor thereof or one of multiple precursor components of a multicomponent adhesive or surface coating, all of which are so sprayed.

If a single fluid precursor, the precursor will react with itself after leaving the sprayhead (generally after external activation) to form the adhesive or surface coating. Multiple precursor components will react or continue to react mutually after leaving the sprayhead(s).

Fluids of interest are more fully discussed hereinafter.

Where a single fluid is sprayed in accordance with the present invention only a single sprayhead is necessary. When a plurality of fluids (for example two) is sprayed, this may be achieved either by

a) multiple single sprayheads arranged so that the e.g. two fluids are mutually contacted in flight or on a substrate surface, or (for adhesives) on separate substrate surfaces which are subsequently contacted together, or

b) a single sprayhead with multiple feeds to a single outlet or to multiple outlets to give pre-flight, point-of-flight or in-flight contact of the fluids.

In use of course the or each sprayhead is charged to a potential different from that of the substrate and the field intensifying electrode the former of which is generally at earth potential. An electrical field is thus set up between the sprayhead and the earthed substrate and the field intensifying electrode, and fluid sprayed from the sprayhead acquires the charge of the sprayhead and is attracted towards any adjacent surfaces at same-sign lower, earth or opposite sign-potential. In general, the field intensifying electrode in its position adjacent to the sprayhead does not affect the field to the extent that it becomes a target. The substrate is generally placed to be the closest earthed surface in the spray 'line of fire' and most, if not all, of the spray will be attracted to impinge on the substrate; in fact spraying parameters may be con-

trolled as described hereinafter so that the spray impinges on only a part of the substrate if desired. In practice, even with non- or semi-conductive substrates, (for example cellulosic, plastics or siliceous substrates) the use of a conventional target (field) electrode behind such substrates is not strictly necessary, unless strict control of the spray pattern is desired (see 'auxiliary electrodes' hereinafter).

In one aspect, the present invention uses an apparatus for the spraying of a fluid (in particular an adhesive or surface coating or a precursor thereof) comprising a sprayhead with a channel for the fluid communicating with an outlet and means for subjecting the fluid to an intense electrical field such that the fluid will move from the sprayhead to form a spray under the influence of the field, the means including means for applying a first potential to the fluid and an electrode mounted adjacent to the sprayhead with means to apply a second potential to that electrode.

Generally a single fluid which reacts with itself after leaving the sprayhead will be sprayed from a single outlet. However, (less usually) a plurality of mutually reactive fluids may be mixed in the sprayhead (e.g. in a mixing chamber) to form a single fluid which is then fed to and sprayed from a single outlet.

When spraying a substrate at earth potential, the first potential may be ± 1 to 20 KV and the second potential may be at or near earth potential, as disclosed in our UK Specification No I,569,707.

The first potential may also be ± 25 to 50 KV, and the second potential ± 10 to 40 KV, as disclosed in applications claiming priority from UK Application No 8432274.

The electrode may comprise a core of conducting or semi-conducting material sheathed in a material of dielectric strength and volume resistivity sufficiently high to prevent sparking between the electrode and the sprayhead and volume resistivity sufficiently low to allow charge collected on the surface of the sheathing material to be conducted through that material to the conducting or semi-conducting core. Suitably, the volume resistivity of the sheathing material is between 5×10^{11} and 5×10^{13} ohm.cm, the dielectric strength of the sheathing material is greater than 15 KV/mm and thickness of the sheathing material is 0.75 to 5 mm, preferably 1.5 to 3 mm. Sheathed electrodes of this form are also disclosed in our co-pending applications claiming priority from UK Application No 8432274.

Sheathed electrodes typically using the latter potentials above are of particular use in spraying at high flow rates (for example spraying pesticides on the land) as disclosed in the reference specification. However, in general in the application of adhesives, and in the application of surface coatings to

relatively small objects such as packaging it is not believed, e.g. that practicable or convenient production line speeds will require such high flow rates, and therefore the use of this particular apparatus embodiment.

Preferably the electrode is adjustably mounted to permit ready variation in relative positions of the sprayhead and electrode.

The spray may be diffused by placing the electrode upstream of the emerging spray or focused by placing it downstream of the emerging spray.

In the above apparatus with single sprayhead(s) the, or each, single sprayhead may have any of the forms conventionally used for the atomisation of a fluid in an electrostatic field. Thus at the end of the feed conduit the sprayhead may have a nozzle orifice (generally circular), an annular slot (for example formed by a circular aperture with a concentric core) or a rectangular slot. Such slots may be curved convexly or concavely along their length. All these apertures are preferably of capillary cross dimensions, e.g. 0.05 to 0.5 mm, to assist atomisation. Similarly, it is preferred that the apertures are defined by sharp edges, which may additionally be toothed, so that the field intensity at the sprayhead surface, and hence the atomisation, is enhanced.

In view of the proximity of electrode to the sprayhead it is often convenient that the electrode follows the shape of the fluid outlets, e.g. twin parallel bars by a slot, or an annulus or torus by a circular nozzle or annular slot.

Atomisation and/or effective spray deposition may in some instances be assisted by a gas stream with (or less usually across) the issuing spray, as in UK.I569707. In some cases this stream may have further advantages, for example, if heated, as a thermal initiator, or for bearing a dispersion of a catalyst or a catalytic initiator and/or promoter, for some free-radical curing adhesives and surface coatings.

In another aspect, the present invention uses an apparatus for the spraying of a plurality of fluids (in particular the precursor components of a multi-component adhesive or surface coating) comprising a sprayhead with a plurality of channels for said fluids each communicating with an outlet, and means for subjecting the fluids at the outlets to an intense electrical field, such that the fluids will move from the sprayhead under the influence of the field to form a spray, the outlets being so disposed that the fluids mix on, or whilst moving from, the sprayhead, in which apparatus the means include means for applying a first potential to at least one of the fluids and an electrode mounted adjacent to the sprayhead with means to apply a second potential to that electrode.

When a plurality of fluids is sprayed from such a single sprayhead with multiple feeds, these feeds may conveniently end in closely adjacent orifices or slots (for example parallel rectangular slots) or a closely adjacent coaxial circular orifice and annular slot(s) or similarly coaxial annular slots. Mixing of the components as sprays occurs at the point of flight, or during flight.

As for single sprayheads, sharp, optionally toothed, edges and a forced gas stream may be advantageous.

Where the feeds end in closely adjacent parallel slots, the feeds are conveniently in the form of channels between parallel plates.

Good mixing of two components is achieved where such a sprayhead comprises four such plates, two inner and two outer, defining three channels. Suitably, the plates are symmetrical about the central channel, the edges of the plates by the outlet slots are chamfered towards the central outlet and the central outlet is located downstream of the two outer outlets, to give a broadly sphenoidal (i.e. wedge-shaped) outlet edge of the sprayhead.

Suitably the included angle of the chamfers or bevels on the inner plates is less than the included angle of the bevels on the outer plates, being respectively preferably in the ranges 10 to 60° and 80 to 150°.

In use one component fluid is run down the central channel, and the other is run down the two outer channels.

A three-plate two-channel sprayhead may also be used, with the central plate having two opposing bevels as described above for the two inner plates, and the sprayhead is also generally sphenoidal.

The edges of the plates may be convexly or concavely curved along their length.

Similarly, where for two components the feeds end in a closely adjacent circular orifice and a coaxial annular slot, these feeds are conveniently in the form of a central tube bore and a channel defined by that tube and a coaxial outer tube interior. Again, good mixing is achieved when the outlet ends of the tubes are symmetrical about the common tube axis and chamfered towards the central outlet and the central outlet is downstream of the outer outlet, to give a broadly conical outlet face of the sprayhead.

Suitable and preferred included angles of the bevelled edges of the tubes are as described for the analogous plates hereinbefore.

In use one fluid component is run down the central channel, and the other is run down the outer channel.

Sprayheads and field intensifying electrodes of this type are described in greater detail in copending applications claiming priority from UK.8504253.

- 5 Considerations of working potentials and the nature, shape and use of the electrode are as for single sprayheads hereinbefore.
- 10 The orientation of any of the above sprayheads in use is in general not critical.
- 15 In all the foregoing sprayheads (single and multiple) suitable means for subjecting the fluids at the outlet(s) to an electrical field include a chargeable, e.g. metal electrode in the sprayhead in contact in use with at least one of the fluids (and preferably both or all) either at the outlet(s) (for example a conducting or semi-conducting sprayhead outlet surface) or a short distance upstream thereof (for example as a buried electrode within a non-conducting sprayhead).
- 20 Any appropriate method of producing the desired potential may be used, for example transformed and rectified mains supplies or a van der Graaf generator.
- 25 The field intensifying electrode may for example be run off an inductive or resistive tap off a transformed mains sprayhead supply.
- 30 Conventional insulation precautions must of course be taken for all points at other than earth potential.
- 35 Under the effect of the electrostatic field, the spray droplets of adhesives and surface coatings produced in accordance with the present invention tend to produce layers on the substrate which are very even and essentially pin-hole free and without occluded air pockets. This is especially useful both for achieving a desirable even adhesive layer which is of good adhesion to maximum substrate surface area and free from blemish, and for producing thick, pin-hole free barrier coatings, e.g. anti-corrosion coatings.
- 40 The average size of the atomised droplets in general may be controlled by the position of the field intensifying electrode in relation to the sprayhead surface. For example, for a given flow rate of liquid, bringing the electrode closer to the sprayhead surface results in the droplets generally being of a smaller average size.
- 45 By controlling the position of the electrode a selected size of droplets may be produced suitable for a particular use. For example, large numbers of small particles (e.g. 20-30 micron diameter) may be preferred for maximum thin coverage of a substrate, larger particles for thicker films.
- 50 The process of the present invention is versatile in that adhesives films as thin as about 1 micron may be applied, as well as thick surface coatings (such as high build coatings) in excess of 1 mm thick.

The enabled use of rapid-reacting systems facilitates the production of high build coatings without sag.

The process of the present invention may be used in application to a wide variety of substrates (including those which may be so treated by contact or conventional spraying methods) to the extent they are compatible with any given adhesive or surface coating. As noted hereinbefore the process is especially useful in connection with continuous production lines whether for piece or continuous substrates. Examples of substrates include the following, which may be piece and/or continuous as will be seen to be appropriate:

packaging, e.g. paper, board, wood, and plastics film and sheet,

sheeting, (including sheeting for processing to packaging, laminates, shoe soles, aero skins and boat hulls, and such processed items), e.g. paper, board, plastics, metals.

textiles, (as pieces or web) e.g. for adhesive dressings,

structural members, (including shoe uppers and aero and boat frames) e.g. plastics and metal,

fibres, e.g. siliceous or plastics optical fibres, tensile fibres, such as fibres for reinforced metal or plastics composites, and textile fibres such as thermoplastics fibres.

It will be apparent that the sprayhead(s) and the substrate may be stationary relative to one another during the spraying, or (any of) the sprayhead(s) and the substrate may move relative to each other during the spraying. Any such movement may be continuous or discontinuous and for only part or all of the spraying process.

It is often convenient to move the substrate past (a) stationary sprayhead(s), especially where the substrate is continuous, although it may be useful for example to move a sprayhead across a continuous elongate substrate; for example the sprayhead may be on a programmable robot arm or gantry.

Similarly, where the substrate is a piece it is often convenient to move each piece on a production line to a spraying position, and thereafter to move (a) sprayhead(s) for application to different parts of the piece.

Where a single sprayhead applies a single fluid or a multiple-feed sprayhead applies several fluids, several such sprayheads spaced apart to avoid mutual electrostatic interference may be used synchronously on different parts of the same substrate, or on different substrates.

Where single sprayheads are used to mix two fluids in flight or on the substrate, mixing in flight clearly requires synchronous spraying of the components; however mixing on the substrate may be effected by synchronous spraying of the same area

of the substrate, or by sequential mixing by sequential spraying to the same area, by synchronous spraying whilst moving a given area from one spray to the other, or in the case of adhesives by separately spraying two substrate surfaces which are subsequently contacted together.

However, we have found that mixing in flight generally gives far more satisfactory mixing of the components leading to more homogenous cure and thus better quality adhesion and surface coating.

The apparatus may also comprise one or more auxiliary electrodes to further influence the spray pattern, without being close enough to the spray-head to affect the spraying potential significantly.

Accordingly in a further aspect, the invention provides a process of the present invention characterised in that the distribution of the electrostatic field is controllably modified by at least one auxiliary electrode as defined.

The shape and location of and relative potential on the auxiliary electrode(s) all affect the spray pattern. A variety of patterns may be achieved in this way, and accordingly these parameters may vary between wide limits, depending as they do on the same parameters inter alia as do the field potential and spraying distance (q.v.), and suitable values may similarly be readily determined by routine trial.

In one of its simplest forms an auxiliary electrode may be a conventional conductive target (field) electrode at for example earth potential and behind the target substrate. Such an electrode will tend to focus the spray into a pattern on the substrate which tends to conform to the shape of the electrode. Relatively complex deposition patterns may be achieved in this manner. Otherwise any auxiliary electrode may be in any suitable shape e.g. straight, curved or annular metal rods, or flat, curved, dished, cylindrical or partly or fully toroidal grids of the same rodding. Such electrodes may be connected in a network at different locations but at the same potential, or may be held at different potentials. For the spraying parameters mentioned hereinbefore, straight, curved or annular steel rods of 1 to 10 mm diameter and 50 to 500 mm in length or annular diameter may be used either singly or arranged to form a planar, curved or cylindrical grid of straight rods, a curved or dished grid of curved rods, or a cylindrical or partly or fully toroidal grid of annular rodging, in each case with a mean spacing of 10 to 100 mm between rods.

Each auxiliary electrode may be at the same potential as, or at a potential intermediate between those of the sprayhead and the substrate; for example a substrate at ±1 to ±20 KV with respect to the sprayhead a field intensifying electrode at the same potential as the substrate and an auxiliary

electrode at ± 0.25 to ± 10 KV, or a substrate at ± 25 to 50 KV with respect to the sprayhead, a field intensifying electrode at ± 10 to 40 KV. This may be achieved by for example running the auxiliary electrode off an inductive or resistive tap off the sprayhead supply, or off a separate supply.

Adhesives and surface coatings sprayed in accordance with the present invention tend to exhibit the well known electrostatic 'wrap-round' effect. In a particular use of auxiliary electrodes, at least one auxiliary electrode is shaped and disposed to further enhance this effect, to improve the coating of for example fibre substrates. This is discussed further hereinafter.

Auxiliary electrodes may be in a relatively complex pattern, parts of which can be controllably activated to vary the deposition pattern as required or according to varying size or shape of the substrate. This may be achieved by switching appropriate electrodes by contacting sensors with a template or the surface to be treated. Such a method is particularly useful for complex and variable deposition patterns e.g. on shoe bodies, aero and boat frames or in 'printing' by spraying.

A wide variety of adhesives and surface coatings may be applied in accordance with the present invention (including application to substrates mentioned hereinbefore). These are generally sprayed as room temperature liquids which are, or solutions, dispersions or suspensions of reactive polymers or polymer precursors as convenient. Any solvent or vehicle may be inert or it may react with the reactive component(s) of the sprayed fluid.

Generally the low shear rate viscosity at the spraying temperature of the sprayed fluid(s) should be less than 40 poise, for example between 0.5 to 5 poise although it is a surprising feature of the present invention that fluids with viscosities in excess of 5 poise (and even in excess of 30 poise) may be satisfactorily sprayed to give good coats.

The spraying temperature of the fluid(s) may be any compatible with the fluid(s) or its/their reaction rate. Temperatures from 0 to 80°C for example 15 to 50°C may be used.

Among multi-(generally two-) component systems which may be applied from multiple single sprayheads or single multiple-feed sprayheads are adhesives and surface coatings, which include barrier coatings (e.g. anti-corrosion coatings for ferrous metals), high-build coatings and mould gel coatings for injection or cold press moulding, inks, and paints for bituminous or cementitious substrates, e.g. for road markings.

One class of materials includes both adhesives and surface coatings based on known polymers or polymer precursors which undergo reaction after leaving the sprayhead(s) or their feeds to a spray-

head, typically by free radical, ionic or group transfer polymerisation or by condensation. Surface coatings of this type include barrier, high-building and mould gel coatings as mentioned hereinbefore.

This class includes acrylics (which are favoured rapid-reaction materials typically with setting/curing/gelling times at ambient temperatures of less than 30 sec and in some cases less than 10 sec), unsaturated polyester-olefinic/acrylic copolymers, polyurethanes and polyureas, heterocycles which include epoxides and lactams, and thiolenes.

The above-mentioned sub-classes of materials include the following:

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Acrylics:

- 20 "Vinylic acids": i.e. monomers and oligomers (including co-oligomers) of unsaturated carboxylic acids, which thus include acrylic, methacrylic and itaconic acids.
- 25 Acrylic esters: monomers and oligomers (including co-oligomers) of mono-and polyols esterified with vinylic acids. These include: esters of alkoxy-and aryloxy-alkanols, e.g. ethoxy-and phenoxy-ethanol; mono-and poly-esters of diols, e.g. ethylene, propylene and hexylene glycols;
- 30 mono-and poly-esters of mono-and poly-alkoxylated diols and triols, e.g. the foregoing ethoxylated with 1-3 oxide residues.
- 35 Polyester acrylics: polyesters with or without olefinic unsaturation in the polymer backbone, typically M.Wt. 200-5000 with terminal vinylic acid ester units capping terminal hydroxy groups. These include the following polyester backbones: straight chain alkanediol-alkanedioic acid esters, e.g. adipic or terephthalic - ethylene/propylene/hexylene glycol/Bisphenol A diol polyesters;
- 40 hydroxylalcanoic acid oligomers, e.g. caprolactone and hydroxybutyric acid oligomers; and polycarbonates, e.g. biphenylene polycarbonates.
- 45 Urethane acrylics: polymer backbones having terminal isocyanate groups capped with hydroxy-substituted vinylic acid ester units, e.g. hydroxy-ethyl/-propyl/-hexyl vinylic acid esters. These include the following polymer backbones:
- 50 di-or tri-functional aliphatic (including alicyclic) and/or aromatic isocyanates, biurets or isocyanurates, or similar oligomers of such isocyanates, e.g. bi/tris-(isocyanatophenyl/cyclohexyl)methane.
- 55 polyurethanes from the above with diols, e.g. ethylene/propylene/hexylene glycol(s);

polyalkoxylated derivatives thereof; and/or polyester diols as for polyester acrylics above. Any of the foregoing may be copolymerised with hydroxyamines or amines to give a ureido-substituted backbone.

Epoxy acrylics: polyether backbones with terminal vinylic acid ester groups as for polyester acrylics above. These include polymer backbones based on Bisphenol A at least bis-alkoxylated (e.g. ethoxylated).

Functionalised acrylics: e.g. copolymers of vinylic monomer species, with hydroxy-substituted vinylic acid ester groups, (e.g. hydroxyethyl/-propyl/-hexyl vinylic acid esters) with vinyl acid ester units capping the hydroxy groups or with epoxy groups. Suitable monomer species include:

unsaturated esters in which the unsaturation may be in the acid or alcohol component, e.g. vinylic acid esters, also including crotonates, such as methyl/butyl acrylate/methacrylate, and vinyl/alkyl esters, such as vinyl acetate; and vinylic acids themselves.

The backbone may contain other monomer species such as vinyl halides or vinylidene dihalides.

All the foregoing acrylics may suitably be free-radical polymerised using a conventional peroxide (e.g. benzoyl peroxide) initiator with an amine accelerator/promoter conveniently by feeding (acrylic + initiator) and (acrylic + promoter) from two sprayheads/feeds, or by thermally activating the spray of (acrylic + initiator) in the spray or on the substrate. Group transfer polymerisation using a conventional silicon-based catalyst (e.g. Me₃SiCN) with a fluoride ion activator may also be used, conveniently by separate (acrylic + catalyst) and (acrylic + activator) feeds.

In all the aforementioned acrylics any solvent or vehicle for the monomer or oligomer may be inert, or it may itself contain vinylic or acrylic functions and so be capable of reaction with the dissolved, dispersed or suspended oligomer. Solvents of the latter type include N-vinylpyrrolidone, vinyl acetate and 'vinylic acid' esters of mono-and polyols such as tetrahydrofuranol and ethylene glycol.

Unsaturated polyesters - olefinic/acrylic copolymers:

Copolymers of polyesters having olefinic unsaturation generally in acid residues/with olefins or vinylic acids or esters. Apt polyester components include straight chain alkenediol-

alkenedioic acid esters. Suitable acids include maleic, fumaric, itaconic and mesaconic acids. Suitable glycols include

ethylene/propylene/hexylene glycols and alkoxylated derivatives thereof and of Bisphenol A. Such polyesters will typically also include saturated comonomers, e.g. saturated acids, such as phthalic, sebacic and/or adipic acids; and hydroxyalkenoic acid oligomers.

Suitable comonomers include those monomer species described for functionalised acrylics above, and styrene and methylated styrenes. Polymerisation may be conveniently effected as described for acrylics above by feeding initiator and promoter from separate sprayheads or feeds with any combination of comonomers therewith.

20 Polyurethanes/Polyureas:

Polyisocyanates with polyols and/or (poly)-olamines as described for urethane acrylics above, and polyamine analogues of these polyols. These react to give polyurethanes or their polyurea analogues.

Polymerisation of the polyurethane precursors may be effected by feeding polyisocyanate from sprayhead or feed and polyol from another. The necessary catalyst, e.g. a tertiary amine or a tin compound such as dibutyltin dilaurate may be fed from either sprayhead or feed.

Polymerisation of the polyurea precursors may be effected analogously without the need for a catalyst.

Heterocycles (including epoxides):

Heterocycles such as: epoxides, e.g. epoxalkylated Bisphenol A derivatives (e.g. epoxyethylated), glycidyl esters and cycloalkene epoxides;

thioepoxides, e.g. thio analogues of the above; lactones, e.g. caprolactone; lactams, e.g. caprolactam; and oxazolines.

Ring-opening and polymerisation of the heterocycle fed from one sprayhead or feed may be catalysed by e.g. an amine or a Lewis or Bronsted acid (e.g. BF₃, H⁺) fed from the other.

Thiolenes:

Unsaturated (olefinic) materials such as described for acrylics and unsaturated polyesters, etc, above, reacting with e.g. (poly)thiols. Virtually any such sulphur species is suitable. Free radical polymerisation may be effected by feeding a peroxide initiator from one sprayhead or feed and an amine promoter from another, with olefin and/or thiol, etc, from each sprayhead or feed.

Free radical polymerisation may be effected by feeding a peroxide initiator from one sprayhead or feed and an amine promoter from another, with olefin and/or thiol, etc., from each sprayhead or feed.

Single component systems which may be applied from single sprayheads include adhesives, and surface coatings which include barrier, high build and mould gel coatings, inks and paints for bituminous or cementitious substrates.

Such single component systems include any material

a) which does not react in or after flight, e.g. solutions of pressure sensitive adhesives, or

b) reacts in or after flight, i.e. any system where reaction is externally initiated at the sprayhead, in flight or on the substrate.

Within category a) pressure sensitive adhesives include conventional acrylic adhesives of this type based on polymers and copolymers of hydroxyalkyl vinylic acid esters.

Within category b) the external initiation may be radiation curing, i.e. by radiation such as microwave, uv, visible, ir, electron beam or sonic, or chemical such as in anaerobic adhesives and (e.g. nitrogen stoving) coatings or by treating the fluid in flight with a catalyst, or catalytic initiator and/or promoter e.g. dispersed in a gas mass or stream in contact with the spray.

Radiation curing systems are essentially free-radical curing systems, which may be initiated in or after flight. All the free-radical adhesives/coatings materials described above for multicomponent systems may be used, i.e. acrylics, unsaturated polyester-olefin/acrylics and thiolenes. Radiation curing systems also include monomer or oligomer precursors of the acrylic pressure sensitive adhesives described above; these are generally cured on the substrate.

The single sprayed fluid will contain all the desired monomers and/or oligomers and a conventional catalyst/initiator which itself is initiated by the relevant radiation. For example, suitable uv curing catalysts include benzophenone-amine systems.

Anaerobic adhesives and coatings are generally cured on the substrate.

All the foregoing adhesives (single or multi-component) may also contain conventional thermoplastic components, e.g. tackifying resins, and surfactant slip agents to promote 'wetting'

5 Figures 1 to 3 hereinafter show various embodiments of an apparatus for the application method of the present invention.

The apparatus shown in Figure 1, for the application of adhesives or surface coatings to flat (e.g. board) substrates, has a sprayhead 1, here comprising a conductive circular capillary nozzle 2 of the type described hereinbefore, and an annular field intensifying electrode 18 of 15 to 25 mm diameter is mounted coaxial with and 20 mm below the nozzle 2. The electrode consists of a core of conducting or semiconducting material sheathed in a material of dielectric strength 15 KV/mm, volume resistivity between 5×10^{11} and 5×10^{13} ohm. cm, and thickness 0.75 to 5 mm.

10 The sprayhead 1 is mounted directly above a flat substrate 3, which may be for example a roughly rectangular piece of cardboard scored and slotted into the knocked down form of a box and on a conveyor belt, or a movable textile web or length of paper strung between and rolled up on drums or axles 4,4 (not shown).

15 Where it is desired to lay down an adhesive pattern on the substrate 3 the sprayhead 1 may be mounted on a programmable robot arm or gantry to enable movement over the substrate 3.

20 A field electrode 5 behind the substrate 3 may be unnecessary, as sufficient control of the spray pattern may be achieved if desired by adjusting the potential, size and configuration of the nozzle 2 and the electrode 18 and their relative positions, and by the use of (other) auxiliary electrodes if necessary. If used, the field electrode 5 is conveniently of the same shape as the desired spray deposit, for example a rectangular metal plate for a strip deposit on a web, or such plates in a pattern for an adhesive pattern on a box).

25 The nozzle 2 is connected via a line 7 containing pump 8 to a reservoir 9 for the material to be sprayed.

30 The apparatus of Figure 1 may be operated as a single nozzle apparatus with only the above-mentioned components, for example for applying a pressure sensitive adhesive or a radiation curing adhesive or

35 In such use, the sprayhead 1 and electrode 18 are charged to the working potentials described hereinbefore. Where the substrate 3 is a movable web, it is set in motion.

40 The spraying fluid, e.g. a polymer solution, is pumped from the reservoir 9 to the nozzle 2 where it atomizes to spray droplets 10 which are charged to a potential of the same sign as the nozzle 1 with

respect to the substrate 3 and are attracted through the annular field intensifying electrode 18 towards the substrate. They impinge on the upper face II of the substrate 3 in a strip I2.

Where the substrate 3 is sprayed with a surface coating the strip I2 will conveniently be adjusted to be the whole of the face II. In the case of a moving web substrate 3 the strip I2 is continuous. In the case of a knocked-down box substrate 3 the sprayhead I is conveniently moved to apply a desired pattern of strips of applied adhesive. The use of the electrode 18 to control the spray pattern has been described hereinbefore, and the optional use of (an) auxiliary electrode(s) also for controlling the spray pattern is described below.

Where the applied fluid is a radiation curing material the apparatus is also provided with a radiation source I3 which as apt may be a uv lamp, an infra-red heater, or a hot gas stream, etc. Where the fluid is a surface coating, it is often convenient for the source I3 to impinge on the substrate 3 either at the point of contact of the spray I0 or at some point to which the coated substrate 3 is moved. Where the fluid is an adhesive, it is clearly desirable to initiate reaction with the source I3 at the sprayhead I or in the spray I0.

The general region of the spraying, i.e. the sprayhead I, electrode 18, spray I0 and substrate 3 may if desired be shrouded by a container I4. This may serve to exclude undesirable drafts and/or to contain an inert, e.g. nitrogen, atmosphere which may be desirable for some reactive fluids. If desired the container I4 may be purged, and/or migration of the spray I0 to the strip I2 on the substrate 3 assisted, by a gas stream within the container which is supplied to the container I4 by a duct I5 and vented via a mouth I7. The gas stream may advantageously assist any inert solvent loss from the spray I0, especially if warm, and such a warm or hot stream may be used as a thermal initiator, for example for adhesives.

Auxiliary electrode(s) 6 (not shown) if used to control the spray pattern may be mounted where apt, for example at the sides of the spraying region which contains the sprayhead I and substrate 3 and/or behind the substrate 3, generally in excess of 80 mm from the sprayhead I.

By judicious choice of potential for example it or they may be used to focus or diffuse the spray I0 onto the substrate 3. (Where a container I4 is present, it may enclose, or itself be used, in whole or in part as, (an) auxiliary electrode(s)).

Once sprayed with a surface coating the substrate 3 is moved from the spraying region and left to cure.

Where the substrate 3 is a knocked-down box sprayed with adhesive, it is generally moved on to conventional packaging assembly apparatus, knocked up into a box, and the sprayed surfaces are contacted with other surfaces of the box and the adhesive is allowed to cure.

Using further components described below, the apparatus of Figure 1 may be used for the analogous application of two component systems in a twin nozzle sprayhead. Thus in this embodiment the nozzle 2 is surrounded by a coaxial annular slot 22 as described hereinbefore, connected via a second line 27 with pump 28 and second reservoir 29 (28 and 29 not shown). Reservoirs 9 and 29 separately contain the two components, for example (acrylic + initiator) in 9 and (acrylic + promoter) in 29. Delivery from the two nozzles may conveniently be in a 1:1 volume rate ratio although any ratio which allows adequate reaction may be used.

In this case of course the radiation source I3 is unnecessary. In all other respects the spraying process is essentially as described for single-nozzle application.

Figure 2 shows a modification of the spraying region of the apparatus of Figure 1 for the application of surface coatings to fibre substrates, for example siliceous or plastics optical fibres. The orientation of the sprayhead I and substrate 3 is immaterial; thus Figures 2a) and 2b) respectively show:

- a plan and end elevation,
- a side elevation and plan, or
- a side elevation and end elevation,

depending on this orientation.

In Figure 2 the modification comprises the same type of sprayhead as in Figure 1 with a single nozzle 2 for single-fluid spraying or twin nozzles 2 and 22 for two-fluid spraying, and the same type of annular electrode 18 mounted as in Figure 1. The sprayhead I is mounted above or to the side of a earthed fibre tow 3, which may itself be essentially horizontal or vertical and supported conventionally. The sprayhead I, the electrode and the fibre tow 3 in the spraying region may be surrounded on three sides by a grid auxiliary electrode 36.

The rest of the apparatus (not shown) is essentially as as described for Figure 1.

In use the fluid(s) are pumped to and atomised at the sprayhead I. The sprayhead I and electrode 18 are charged to the working potentials described hereinbefore, and the fibre tow 3 is drawn through the spraying region.

Because of the 'wrap around' effect found in electrodynamic spraying it may be possible by adjusting the nozzle 2 and electrode 18 potentials, sizes and configuration and the relative positions of these and other parts of the apparatus and the fibre 3 to achieve adequate coating around a good part

of the fibre periphery. If not, or if more even coating is required, the sprayhead 1 may be a single or multiple slot (2 or 2, 22, 22¹) sprayhead at right angles to the tow 3 and curved concavely and coaxially with the tow 3 (with a corresponding shaped twin-bar electrode 18), or the auxiliary electrode 36 may be used and the potential on it adjusted so that the spray 10 fans out as shown to curl around the fibre to points not facing the spray-head 1.

Additionally to use of the auxiliary electrode 36, a similar or identical sprayhead 31 and field intensifying electrode 48 may be placed further along the fibre tow 3 on the opposite side of the fibre 3 from, and well spaced from, the first sprayhead 1 to augment the coating where it is deficient or absent.

Figure 3 shows a two-sprayhead apparatus for the separate application of the two components of a two component system to flat (e.g. board) substrates. It will be seen that it is generally similar to the apparatus of Figure 1, and the type of substrate 3 and its feed to the apparatus is the same.

The apparatus of Figure 3, however, has two separate sprayheads 1 and 31 comprising conductive circular capillary nozzles 2 and 32 respectively, with electrodes 18 and 48 respectively. These are mounted far enough apart that in use there is no deleterious interaction of their electrostatic fields to earth. As shown they are mounted above and to either side of a textile web substrate 3 or a conveyor belt for substrate pieces 3, and are aligned upon a favoured mixing region immediately above the substrate 3. However, as noted hereinbefore the two components may also be mixed on the substrate 3 by synchronous or sequential spraying to the same part of the substrate, by synchronous spraying to different parts of the same substrate which are moved from one spray to the other, or in the case of adhesives by spraying each component onto separate surfaces of the substrate 3 which are to be adhered. Suitable arrangement of the sprayheads 1 and 31 for these purposes will be clear to the skilled man. In general maximum spatial separation of the sprayheads 1, 31 will tend to minimise undesirable field interactions.

Sequential spraying to the same part of the substrate may be advantageous as the fields of the two sprayheads 2 and 32 may be switched alternately. Similarly, synchronous spraying to different parts of the substrate 3 which are moved from one spray to the other may be advantageous as the fields of the sprayheads 2 and 32 may be spatially well separated. Both methods offer the advantage of avoiding potentially deleterious field interactions.

Mixing of sprays 10 and 40 if of the same charge sign may not be entirely satisfactory. Accordingly, to achieve better mixing it may be desirable in use to have each sprayhead 10 and 40 of different polarity with respect to earth, provided that the application of the spray is not adversely affected thereby. Additionally the polarity of the sprayheads may be simultaneously reversed or alternated.

Other features of the apparatus, such as programmable means to move the sprayheads 1, 31, associated lines 7, 37, pumps 8, 38 and reservoirs 9, 39 for the two component fluids, and associated optional auxiliary electrodes 6 and 36 (all omitted) are essentially the same as in Figure 1. There is of course no necessity for any radiation source 13.

The use of the apparatus is essentially as described for Figure 1 twin nozzle application, except that application of the two components may be synchronous or sequential. Thus, e.g. the reservoirs 9 and 39 may separately contain (acrylic + initiator) and (acrylic + promoter).

In connection with Figure 2, the synchronous spraying of different parts of a fibre tow 3 which are moved from one spray 10 to a second spray 40 has been described in relation to single nozzle single fluid and twin nozzle spraying. Clearly the same type of arrangement may be used for two nozzle two component spraying. It will be apparent how such an arrangement may be further modified to achieve in flight mixing and synchronous and sequential application to the same part of the fibre tow 3.

The invention is further illustrated by the following Examples:

Typical spray rates in the following Examples are in the range of 1 to 3 cm³/sec/mm of slot nozzle.

EXAMPLE 1

Using an apparatus as described in Figure 1, but with a single slot nozzle, four Q panel type S (ground face) steel sheets were coated with four different sprays based on two urethane methacrylate resins in two reactive solvents, and also containing 2% w/w benzophenone-amine photoinitiator and 0.5 % w/w surfactive slip agent. (Ebecryl 350 - acrylated siloxane). The coats were all in excess of 100 micron thick, and were removed from the spraying region and u.v. cured. Curing times were approximately 4 min at room temperature.

The resins all consisted of an aromatic urethane oligomer backbone (optionally extended with a polyethylene oxide chain) having terminal isocyanate functions capped with 2-hydroxyethyl methacrylate, and are Modar 804, 805 and 806. (ICI TM).

The two reactive solvents used were: ethyleneglycol dimethacrylate (EGDMA) and triethyleneglycol dimethacrylate (TEGDMA).

Spray solution viscosities (Brookfield, 20°C) were in the range 0.8 to 7.2 poise. Surprisingly, the apparatus could be used to spray a TEGDMA 805 solution with a viscosity of 7 poise.

EXAMPLE 2

Using the apparatus, solvents, solvent proportions and procedure of Example 1, printed card sheets were coated with a 5 micron thick u.v.-cured coat based on an ICI Bisphenol-A epoxy acrylate resin, to give a smooth overprint varnish.

Methacryloxyethyl phosphate (1 to 3% w/w) (adhesion promoter) was added to B in further spray coating of steel sheet in the above manner with no deleterious effect.

EXAMPLE 5

a) Using the apparatus of Example 3 with two board substrates on the belt, the two substrates were coated to 30 micron thickness with a urethane acrylate resin in two different reactive solvents, viz an aliphatic (isophorone) diisocyanate-polypropylene diol (M.Wt. 1200) urethane resin with terminal isocyanate functions capped with 2-hydroxyethyl acrylate (50% w/w) or a mixture of ethoxethoxyethyl acrylate and 1,2,3-trimethylolpropane triacrylate (1:1 w/w) (50% w/w) as:

- A: 1% w/w BPO
- B: 1½% w/w DMPT.

(The respective gel times of the two systems were: 14 sec and 22 sec).

The coated board in each case was rapidly removed from the spraying region and immediately overlapped with an identical but untreated board.

Adhesion occurred after the appropriate gel time, when on pulling the boards apart, severe delamination of the board fibres rather than adhesive layer break was observed.

b) The procedure of a) above was repeated using the above solution in 2-hydroxyethyl acrylate solvent but with further BPO as:

EXAMPLE 3

Using an apparatus as described in Figure 1 but with a triple slot twin nozzle of the type described hereinbefore, a brown paper belt between a motorised wind-up roller and a feed roll was coated continuously with Modar 804 in EGDMA (40% w/w solution with 100 ppmw benzoquinone (viscosity - Brookfield, 20°C - 2.3 p). Equal volumes A, B of the above were placed in the two reservoirs (9 and 29 in Figure 1) with the following additives:

- A: 4% w/w benzoyl peroxide (BPO)
- B: 1.2% w/w N,N-dimethylparatoluidine (DMPT) and 2% w/w surfactant (Ebecryl 350).

The two components were sprayed at equal flow rates.

For the coats, gel time was about 45 sec and gel to peak 45 sec.

EXAMPLE 4

Using the apparatus of Example 3 with steel and glass sheet piece substrates on the brown paper belt, the steel and glass sheet was coated in the manner of Example 2 with a urethane acrylate (similar to 804 and 805), ICI reference 835 (contains 13% w/w Daltocel F2805 polyether triol as a chain extender) in tetrahydrofuryl methacrylate (50% w/w) solution (viscosity - Brookfield, 20°C - 4.0 poise) as: A: 3% w/w BPO
B: 1% w/w DMPT and 2% w/w Ebecryl 350.

Cure times for the coatings were about 4 minutes.

- A: 2% w/w BPO
- B: 1½% w/w DMPT with a gel time of 7 to 9 sec.

On overlapping with and pulling apart from another board, after the gel time, severe delamination of the board fibres rather than adhesive layer break was observed.

EXAMPLE 6

Using an apparatus as described in Figure 3 with two single slot nozzles set up to spray in two spatially discrete regions, two board substrates were sprayed separately with 30 micron coats of the 2-hydroxyethyl acrylate solutions A and B of Example 5a).

On overlapping the boards and pulling them apart after the 14 sec gel time, noticeably less good board delamination than in Example 5a) was observed.

The procedure was repeated with the other A and B solutions of Example 4a) with observation of the same effect on adhesive bond strength.

Claims

1. A process for the spray application of a fluid which is an adhesive or surface coating or a precursor thereof, characterised by supplying such a fluid to a sprayhead and applying an intense electrical field to the fluid such that the fluid moves from the sprayhead under the influence of the field to form a spray, the field being intensified by means of a charged electrode adjacent to the sprayhead. 5

2. A process according to claim 1 wherein the fluid is a mixture of a plurality of fluid precursor components of a multi-component adhesive or surface coating. 10

3. A process according to claim 1 wherein the fluid comprises at least one but not all the components of a multi-component adhesive or surface coating. 15

4. A process according to claim 1 wherein the fluid reacts with itself or another fluid in or after flight. 20

5. A process according to claim 1 wherein the reaction is initiated by radiation. 25

6. A process according to claim 1 wherein the fluid comprises a polymer or polymer precursor which contains unsaturated carboxylic acid monomer units. 30

7. A process according to claim 1 for the spray application of a plurality of fluid precursor components of a multi-component adhesive or surface coating characterised by supplying such fluids to the outlets of a sprayhead with a plurality of outlets, applying an intense electrical field such that the fluids move from the sprayhead under the influence of the field to form a spray, and allowing the fluids to mix on or whilst moving from the sprayhead, the field being intensified by means of a charged electrode adjacent to the sprayhead. 35

8. A process according to claim 7 wherein the fluids react in or after flight. 40

9. A process according to claim 7 wherein the reaction is initiated by a catalyst or a catalytic initiator and/or promoter. 45

10. A process according to claim 1, characterised in that the electrode comprises a core of conducting or semi-conducting material sheathed in a material of dielectric strength and volume resistivity sufficiently high to prevent sparking between the electrode and the sprayhead and volume resistivity sufficiently low to allow charge collected on the surface of the sheathing material to be conducted through that material to the conducting or semi-conducting core. 50

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Fig. 1.

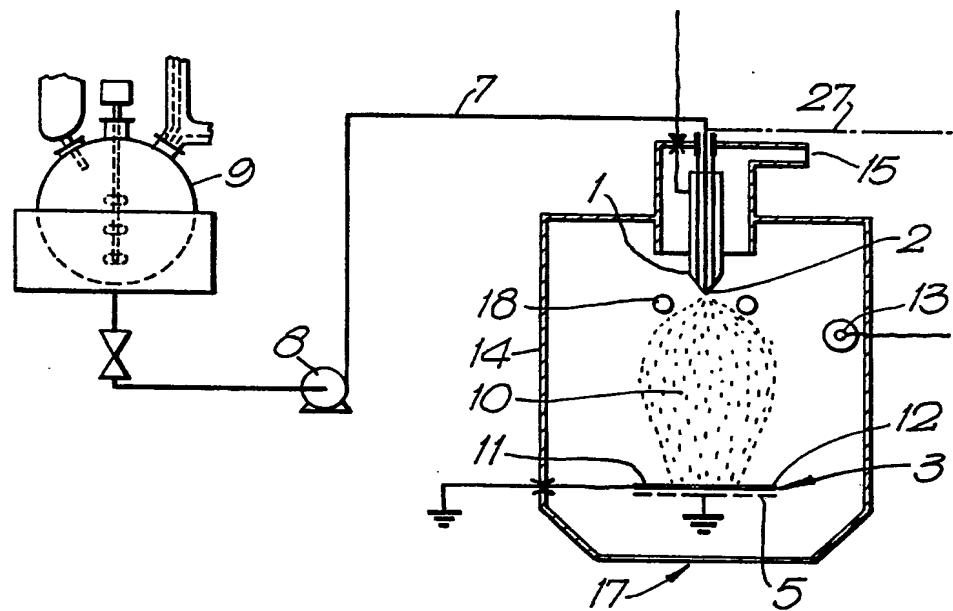


Fig. 2a.

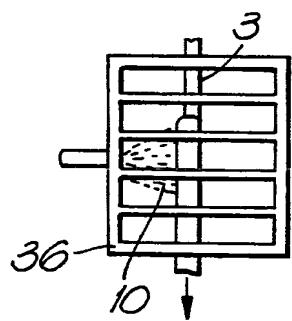
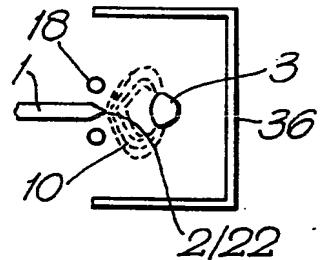
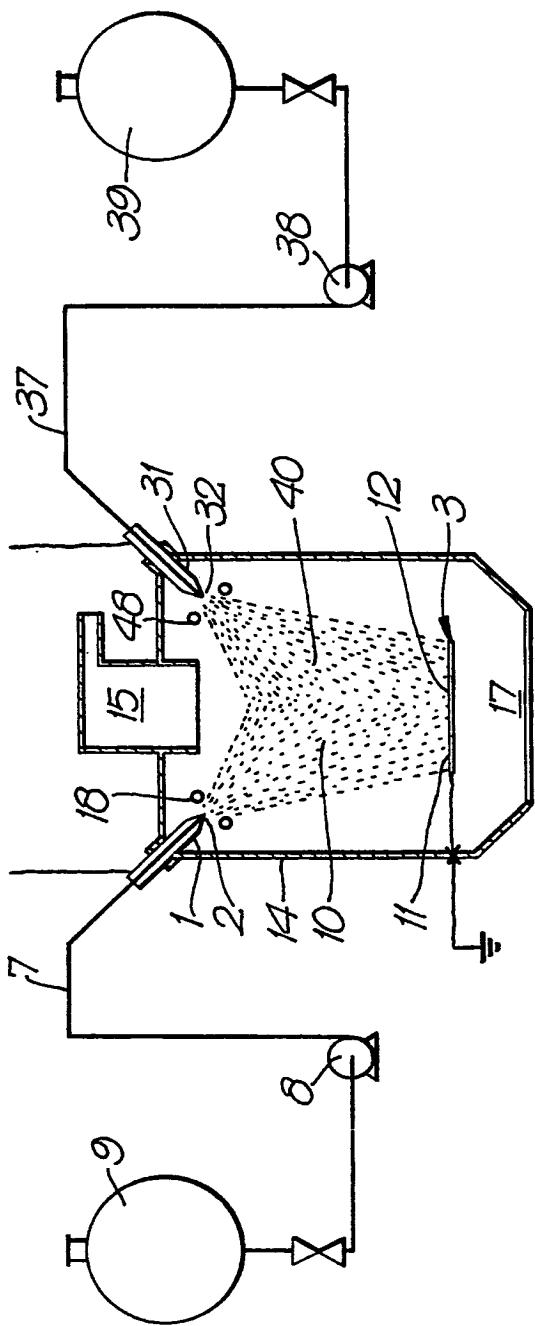


Fig. 2b.



0 253 539

Fig. 3.





European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 87 30 5828

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D, Y	EP-A-0 186 983 (IMPERIAL CHEMICAL INDUSTRIES) * Whole document * ---	1,2,7,8 ,10	B 05 B 5/08
Y	FR-A-1 422 084 (TECHNIGAZ) * Page 3, left-hand column, line 8 - right-hand column, line 12; figures 1-4 *	1,2,7,8 ,10	
A	US-A-4 508 265 (JIDO) ---		
A	US-A-4 383 767 (JIDO) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			B 05 B
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	31-05-1988	JUGUET J.M.	
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